PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : F41H 1/02 — A1

(11) International Publication Number: **WO 00/08411**

(43) International Publication Date: 17 February 2000 (17.02.00)

(21) International Application Number: PCT/EP99/05574

(22) International Filing Date: 30 July 1999 (30.07.99)

(30) Priority Data:
98114608.7 4 August 1998 (04.08.98) EP

(71) Applicants *(for all designated States except US)*: ARAMID PRODUCTS GMBH [DE/DE]; Kasinostrasse 19–21, D–42097 Wuppertal (DE). FMS ENTERPRISES LTD. [IL/IL]; P.O. Box 18077, 61180 Tel Aviv (IL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: FUCHS, Yuval [IL/IL]; Raines Street 35, 42475 Netanya (IL). BÖTTGER, Christian [DE/DE]; Geschwister Scholl–Strasse 25, D–42897 Remscheid (DE). FELS, Achim [DE/DE]; Adalbert–Stifter–Weg 8, D–42109 Wuppertal (DE).

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept AIP), P.O. Box 9300, NL–6800 SB Arnhem (NL).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: STAB RESISTANT MATERIAL

(57) Abstract

Stab–resistant material made from at least two woven fabrics joined together via a polymer film, whereby the fabrics comprise yarns with a tensile strength of at least 900 MPa and the polymer film joining the fabrics has a tensile strength of at least 10 MPa, characterized in that the polymer film joining the fabrics has a flexural modulus of 1500 to 4500 MPa.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

Stab resistant material

The invention relates to a stab-resistant material made from at least two woven fabrics joined via a polymer film, whereby the woven fabrics consist of yarns with a tensile strength of at least 900 MPa and the polymer film joining the fabrics has a tensile strength of at least 10 MPa; a stab-resistant package; and use of the stab-resistant package for making protective clothing.

A stab-resistant material of this type is known from WO 97/21334, whereby the polymer film described therein is to have a flexural modulus of 42 to 1000 MPa. From the examples of this publication, clearly 38 to 45 layers of this stab-resistant material are required to provide stab protection that the specification considers to be sufficient. The evaluation of the stab-resistant quality is reportedly performed in accordance with CEN/TC 162/WG 5 N 479. According to this standard, two different knives are to be used, whereby penetration of each knife up to 20 mm is regarded as sufficient stab protection. Which knife was used in WO 97/21334 is not apparent. Due to the clearly required high number of layers of the stab-resistant material, reduced wearing comfort results if protective clothing is manufactured using this stab-resistant material, since the large number of layers makes the clothing both very heavy and stiff.

The problem remains of providing a stab-resistant material of the type cited initially that offers improved wearing comfort compared to that of prior art stab-resistant materials. The problem also exists of improving the effectiveness of stab-resistant materials.

According to the invention, it has now been discovered that, with a stab-resistant material made from at least two woven fabrics joined via a polymer film, whereby the fabrics are made from yarns with a tensile strength of at least 900 MPa and the polymer film joining the fabrics has a tensile strength of at

least 10 MPa, the effectiveness is significantly improved if the polymer film joining the fabrics has a flexural modulus of 1500 to 4500 MPa.

Surprisingly, it has been discovered that, when using such a polymer film, significantly fewer layers are required to provide effective stab protection than in the case of prior art stab-resistant materials.

It is advantageous if the polymer film has an elongation at break of at least 80%, for example 100% or 120%.

As is also the case in WO 97/21334, the flexural modulus in the present invention is to be determined in accordance with ASTM D-790, the tensile strength of the film in accordance with ASTM D-638, the elongation at break in accordance with ASTM D-638, and the tensile strength of the yarn in accordance with ASTM D-885.

It has proven especially favorable for the stab-resistant material of the invention to comprise two woven fabrics laminated via the polymer film.

Preferably, the yarns forming the woven fabrics have a tensile strength of 900 to 8000 MPa. It has proven particularly advantageous for the yarns forming the fabrics to have a tensile strength of 1500 to 6000 MPa, in particular 3000 to 6000 MPa. In this respect, practically all yarns suited for use in ballistic protection, such as yarns made from polyolefin, in particular polyethylene, from polyamide, polyimide, polyester, or poly (p-phenylene-2,6-benzobisoxazole). Yarns made from aramides have proven especially favorable.

With the stab-resistant material of the invention, it has proven especially advantageous if the polymer film joining the fabrics has a flexural modulus of 1500 to 4500 MPa, in particular from 2000 to 3000 MPa. Suitable polymers are hard PVC, with a flexural modulus between 3500 and 4000 MPa, or polyurethanes with a flexural modulus between 4000 and 4500 MPa.

Polycarbonates have proven particularly favorable. Such a polycarbonate, for example, is marketed under the name LEXAN 103 by GE Plastics. LEXAN 103 has a flexural modulus of 2500 MPa, a tensile strength of 70 MPa, and an elongation at break of 120%.

For the fabrics used for the stab-resistant material of the invention, it has proven most satisfactory for them to have a plain weave, especially if they have a fabric density, calculated according to Walz, of 25 to 80%, preferably 25 to 60%.

The fabric density according to Walz is calculated according to the following formula:

$$DG = (d_k + d_s)^2 \cdot f_k \cdot f_s$$

where

d_k = substance diameter of the warp yarn in mm

d_s = substance diameter of the weft yarn in mm

f_k = warp threads per cm

f_s = weft threads per cm

The substance diameter d_k or d_s of the yarns is calculated as follows:

$$d = (\text{titer})^{1/2} / 88.5 \cdot (\text{density})^{1/2}$$

where d is either d_k or d_s, the titer of the corresponding yarn is in dtex, and the density of the yarn is in g/cm^3.

The values given above apply in particular to fabrics with plain weave. If other than plain weaves apply, a weave correction factor must be included in the calculation. For this weave correction factor, the following values are used for fabrics with specific weaves:

Weave	Weave correction factor
Hopsack weaves 2:2	0.56
Twill weaves 2:1	0.70
Twill weaves 2:2	0.56
Twill weaves 3:1	0.56
Twill weaves 4:4	0.38
Satin 1:4	0.49

The fabric density DG calculated according to the Walz formula is multiplied by these correction factors.

The fabric density DG according to Walz is a quantity expressed in %. In the case of highly dense fabrics, values can exceed 100%.

The stab-resistant material of the invention is optimally suited for manufacturing stab-resistant packages that have multiple layers of the stab-resistant material of the invention. It is especially favorable for a stab-resistant package of the invention to have 6 to 30, preferably 10 to 25 layers of the stab-resistant material of the invention and possibly additional layers made from other materials. For improved handling, it is advantageous if, in the stab-protection package of the invention, several or all layers are positioned in an envelope made from a textile material.

The stab-resistant package in accordance with the invention is optimally suited for manufacturing protective clothing.

The invention will be explained in more detail on the basis of the following examples:

Woven fabrics were manufactured in plain weave from aramide yarns with a titer of 840 dtex and a tensile strength of 3600 MPa. The fabric density

according to Walz was 46%, the weight of the fabrics 215 g/m^2. Positioned between two fabrics was a polymer film made from polycarbonate (LEXAN 103), with a specific weight of 135 g/m^2. The lamination of the two fabrics with the polymer film was performed in a temperature range of 220 to 230°C and a pressure of about 10 bar. Various numbers of these laminates were placed into an envelope made from polyamide woven fabric and the penetration depth of knives 1 and 2 (an English (no.1) and a German knife) determined in accordance with CEN/TC 162/WG 5 N 479. When the stab-resistant package consisted of 8 laminates, there was penetration of only 10 mm with knife 1. When as few as 10 laminates were used in the envelope, no penetration was noted with knife 1, while a penetration of 25 mm was noted with knife 2. After 15 laminates had been arranged one on top of the other in the envelope, there was penetration of only about 5 mm with knife 2, while penetration by knife 1 was no longer noted. With knife 1, it was even observed that the tip of the knife was bent after the test. In the case of 20 laminates in the envelope, penetration was no longer noted with knife 2 either.

In a further test, woven fabrics were produced from aramide yarns with a titer of 840 dtex and a tensile strength of 3600 MPa in plain weave. The fabric density according to Walz was 30% and the fabric weight 170 g/m^2. A polymer film made from polycarbonate (LEXAN 103) with a specific weight of 135 g/m^2 was positioned between two fabrics. The lamination of the two fabrics with the polymer film was performed in a temperature range of 220 to 230°C and a pressure of about 10 bar. Various numbers of these laminates were placed into an envelope made from polyamide woven fabric and the penetration depth of knives 1 and 2 (an English (no.1) and a German knife) determined in accordance with CEN/TC 162/WG 5 N 479. When the stab-resistant package consisted of 8 laminates, there was a penetration of only 10 mm with knife 1 (average value). When as few as 10 laminates were used in the envelope, penetration was no longer noted for knife 1, while the requirements of the standard had not been met for knife 2. After 15 laminates had been arranged one on top of the other in the envelope, there was a penetration of only about

10 mm with knife 2, while again penetration was no longer noticeable with knife 1.

Claims:

1. Stab-resistant material made from at least two woven fabrics joined together via a polymer film, whereby the fabrics comprise yarns with a tensile strength of at least 900 MPa and the polymer film joining the fabrics has a tensile strength of at least 10 MPa, characterized in that the polymer film joining the fabrics has a flexural modulus of 1500 to 4500 MPa.

2. Stab-resistant material according to Claim 1, characterized in that it comprise two fabrics laminated together via the polymer film.

3. Stab-resistant material according to Claim 1 or 2, characterized in that the yarns forming the fabrics have a tensile strength of 900 to 8000 MPa.

4. Stab-resistant material according to one or more of Claims 1 to 3, characterized in that the polymer film joining the fabrics has a flexural modulus of 2000 to 3000 MPa.

5. Stab-resistant material according to one or more of Claims 1 to 4, characterized in that the fabrics have a plain weave.

6. Stab-resistant material according to one or more of Claims 1 to 5, characterized in that the fabrics have a fabric density, calculated according to Walz, of 25 to 80%.

7. Stab-resistant material according to one or more of Claims 1 to 6, characterized in that the polymer film joining the fabrics consists of a polycarbonate.

8. Stab-resistant package containing a plurality of layers of the stab-resistant material according to one or more of Claims 1 to 7.

9. Stab-resistant package according to Claim 8, characterized in that it contains 6 to 30 layers of the stab-resistant material according to one or more of Claims 1 to 7 and possibly additional layers.

10. Stab-resistant package according to Claim 9, characterized in that it contains 10 to 25 layers of the stab-resistant material according to one or more of Claims 1 to 7.

11. Stab-resistant package according to one or more of Claims 8 to 10, characterized in that a plurality of layers or all layers are arranged in an envelope made from a textile material.

12. Use of the stab-resistant package according to one or more of Claims 8 to 11 for manufacturing stab-resistant clothing.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/05574

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F41H1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F41H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	WO 97 21334 A (E.I. DU PONT DE NEMOURS) 12 June 1997 (1997-06-12) cited in the application abstract page 2, line 11 - line 15; claims 1,2,7,15	1
A	US 5 001 003 A (MAHR) 19 March 1991 (1991-03-19) column 2, line 25 -column 4, line 15	1
A	US 4 738 893 A (GRILLO) 19 April 1988 (1988-04-19)	

[ ] Further documents are listed in the continuation of box C

[X] Patent family members are listed in annex

Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 January 2000	21/01/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340 2040, Tx. 31 651 epo nl Fax (+31-70) 340-3016	Van der Plas, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter onal Application No
PCT/EP 99/05574

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9721334 A	12-06-1997	CN 1202237 A	16-12-1998
		EP 0862722 A	09-09-1998
US 5001003 A	19-03-1991	NONE	
US 4738893 A	19-04-1988	FR 2588073 A	03-04-1987
		CA 1277528 A	11-12-1990
		EP 0221794 A	13-05-1987
		ES 2001306 A	01-05-1988